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मानक

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IS 5302 (1969): Code of safety for acetic anhydride [CHD 8: Occupational Safety, Health and Chemical Hazards]



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Indian Standard

CODE OF SAFETY FOR ACETIC ANHYDRIDE

UDC 661.731.4:614.8



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INDIAN STANDARDS INSTITUTION
MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
NEW DELHI 1

AMENDMENT NO. 1 DECEMBER 2006
TO
IS 5302 : 1969 CODE OF SAFETY FOR ACETIC
ANHYDRIDE

[*Page 4, clause 3.1(h)*] — Substitute the following for the existing:

'Flash point (closed cup): 54°C'

[*Page 4, clause 3.1(m)*] — Insert the following at the end:

- 'n) Molecular formula: $C_4H_6O_3$
- p) Molecular weight: 102.09
- q) Vapour pressure: 4 mm of Hg at 20°C
- r) Odour threshold: 0.1 ppm
- s) Auto-ignition temperature: 316°C'

Indian Standard

CODE OF SAFETY FOR ACETIC ANHYDRIDE

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Indian Standard

CODE OF SAFETY FOR ACETIC ANHYDRIDE

0. FOREWORD

0.1 This Indian Standard was adopted by the Indian Standards Institution on 31 July 1969, after the draft finalized by the Chemical Hazards Sectional Committee had been approved by the Chemical Division Council

0.2 Acetic anhydride, also called acetyl oxide and ethanoic anhydride in chemical literature, is represented by the formula $\begin{matrix} \text{CH}_3\text{CO} \\ \text{CH}_3\text{CO} \end{matrix} > \text{O}$. It is an important industrial chemical, used in the manufacture of cellulose acetates, acetyl salicylic acid, polymers, dye intermediates, pharmaceuticals and organic acetates. The reagent grade is a valuable laboratory chemical used for preparative and analytical procedures.

0.2.1 A complete knowledge and understanding of the hazards of acetic anhydride is essential for its safe handling. This standard attempts to guide the users in the recognition of these hazards and in the recommended handling procedures. The information given should be utilized to the fullest extent and should be supplemented with additional information on design aspects of plants and equipment.

0.3 In the preparation of the standard, considerable assistance has been derived from the Safety Data Sheet No. SD-15 'Acetic anhydride' published by Manufacturing Chemists' Association, U.S.A.

1. SCOPE

1.1 This code describes the properties of acetic anhydride, the nature of hazards associated with it and essential information on storage, handling, packing, labelling, waste disposal, cleaning and repair of tanks and equipment, selection and training of personnel, personal protective equipment and first-aid.

1.1.1 This standard does not deal with specifications for design of buildings, chemical engineering plants, storage vessels, and various safety equipment.

2. TERMINOLOGY

2.1 For the purpose of this standard, the definitions given in IS : 4155-1966*, shall apply.

3. PROPERTIES OF ACETIC ANHYDRIDE

3.1 Some of the important physical and chemical properties of acetic anhydride are:

a) Physical state	Liquid
b) Colour	Colourless
c) Odour	Pungent, irritating, acidic smell
d) Boiling point at 760 mm Hg	140°C
e) Explosive limits, percent by volume in air	2.9 to 10.3
f) Relative density at 20°/4°C	1.082
g) Freezing point	-73.1°C
h) Flash point:	
1) Open cup	64°C
2) Closed cup	49°C
j) Solubility	12 percent (w/w) in cold water
k) Corrosivity	Corrodes iron, steel and certain other metals at normal atmospheric temperatures, due to reaction with water to form acetic acid
m) Reactivity	Reacts with steel, lead, tin and cast iron. Reacts with water to produce acetic acid. At higher temperature the reaction is faster. Mineral acids catalyze the hydrolysis. Reacts vigorously with oxidizing material

*Glossary of terms relating to chemical and radiation hazards and hazardous chemicals.

4. HAZARDS ASSOCIATED WITH ACETIC ANHYDRIDE

4.1 Health Hazard

4.1.1 General — Acetic anhydride is a local irritant and is capable of causing severe eye burns. If the liquid is held in contact with the skin by clothing, it is capable of causing burns. The vapour is particularly irritating to the eyes, nose, throat, and upper respiratory tract. The threshold limit value of acetic anhydride is 5 parts per million by volume in air or 20 mg per cubic metre of air.

4.1.2 Acute Toxicity

4.1.2.1 Local — Acetic anhydride does not cause a severe burning sensation upon contact with the skin. In case it is not removed by washing, the skin will become reddened and later will turn white and wrinkled, but may not be painful. In some cases such a burn may be followed by peeling of the skin.

The liquid or vapour is especially hazardous to the eye and may produce a serious eye burn. Immediately on contact, there is a burning sensation with watering of the eyes which may be followed later by an impairment of vision. Acetic anhydride is also capable of causing severe eye burns by delayed action.

4.1.2.2 Systemic — Specific general systemic effects have not been reported. Since the marked irritating properties of vapours afford good warning properties, generalized systemic effects are not likely to occur. Exposure to the vapours results in coughing and a burning sensation in the nose and throat. Exposure to high concentrations of the vapours can result in severe lung damage.

4.1.3 Chronic Toxicity

4.1.3.1 Chronic systemic poisoning has not been reported from repeated exposures to acetic anhydride. Its irritating properties preclude such an effect.

Repeated and prolonged contact of the skin with even low concentrations of acetic anhydride may result in chronic skin irritation. Repeated exposures to the vapour can result in chronic eye irritation.

4.2 Fire and Explosion Hazards

4.2.1 Acetic anhydride is a readily combustible liquid. Its vapour forms explosive mixtures with air over a fairly wide range of concentrations. The vapours are considerably heavier than air and will therefore accumulate in low parts. Explosion hazards are created when impurities are accidentally

introduced into acetic anhydride in a closed vessel. Water is the impurity most likely to be encountered. Even though water is only partially miscible with acetic anhydride and its reaction rate is usually quite low, extreme heat and pressure may be developed in closed vessels when water is inadvertently introduced into the acetic anhydride.

5. STORAGE

5.1 Indoor Storage

5.1.1 Acetic anhydride is a readily combustible liquid, and as such introduces a potential fire hazard where it is stored, handled or used. Fire-proof construction is recommended for all storage areas (*see 4.2*). For small fires use carbon dioxide, dry chemicals or alcohol foam.

5.1.2 Ventilation should be provided at the floor level, as well as in the usual higher locations. Do not store in pits, depressions, basements, or in unventilated areas. Acetic anhydride vapour is 3.52 times heavier than air (*see 3.1*).

5.1.3 All storage areas should be provided with automatic sprinklers or some other adequate fire-extinguishing system desirable on interior storage.

5.2 Bulk Storage

5.2.1 Suitable metals for storage tanks and other equipment include copper, aluminium, stainless steel and some other special alloys. Resin-lined steel tanks are frequently used.

5.2.2 In bulk storage, where adequate spacing and segregation are not maintained, protection against exposure fires, such as automatic sprinklers or water-spray systems, shall be provided.

6. HANDLING

6.1 General—Because acetic anhydride is a readily combustible liquid, railroad locomotives and automotive equipment capable of causing ignition should be excluded from the dock or vapour areas during both unloading and loading operations.

6.2 Spills and Leaks

6.2.1 Frequent equipment inspections should be made to detect and prevent leaks.

6.2.2 Spills should be flushed away promptly with water.

6.2.3 If leaks or spills occur, only properly protected personnel should remain in the area. Leaking containers should be removed to the outdoors or to an isolated, well-ventilated area, and the contents transferred to other suitable containers.

6.3 Small Containers—In most cases, samples will be in glass or polyethylene bottles or in lined metal pails. These should be handled as for an acid, and should be kept closed at all times except when contents are poured. Care should be exercised to prevent contamination with other reactive materials.

6.4 Drums

6.4.1 Each shipment should be examined carefully for leaking drums. If any are found, they should be handled with particular care. The leaking part should be turned up, the drums removed to a safe place for repairs and the contents transferred to a sound container.

6.4.2 Drums should be handled carefully to and from their place of storage. Before emptying contents, substantially support the drums and block them to prevent movement.

6.4.3 Emptying of Drums—To remove the plug from a drum of acetic anhydride the operator should wear goggles, face shield, rubber gloves and rubber apron, and use a bung or plug wrench. He should place the bung up, stand to one side, and face away during the operation. After the plug starts to loosen, it should be given not more than one full turn. If internal pressure exists, it should be allowed to escape to the atmosphere. Then only should the operator loosen the plug further and remove it.

6.4.3.1 The preferable safe method for emptying drums is by hand pump, or electrical pumps with totally-enclosed flame-proof and explosion-proof motors. If drums are emptied by gravity, the faucets should be self-closing. The use of pressure for emptying drums is not recommended.

6.5 Tank Cars

6.5.1 General—Supplier's instructions for unloading should always be followed, and all caution markings on both sides of tank or dome should be read and observed.

6.5.2 Cars should be spotted accurately on a level track. Brakes shall be set and wheels blocked on all cars being unloaded.

6.5.3 Unloading — Tank cars should be electrically bonded to the ground to dissipate static or secondary charges induced by lightning.

6.5.3.1 Before the manhole cover is removed or the outlet valve is opened, the tank car should be relieved of all internal pressure.

6.5.3.2 Tank cars should be unloaded by means of an approved pump through the dome connection rather than through the bottom outlet. The tank car should be vented to prevent collapse, using system vapours (preferably) or oxygen-free gas to replace the liquid withdrawn.

6.5.3.3 If it is necessary to discontinue unloading a tank car for any reason, all unloading connections shall be disconnected. All valves shall first be tightly closed, and the closures of all other openings securely applied.

7. PACKING AND LABELLING

7.1 Packing — Acetic anhydride is packed in glass or polyethylene bottles or carboys. Drums are usually of aluminium, stainless steel, or resinsided steel.

7.2 Labelling

7.2.1 Each container (including tank cars) shall carry an identifying label or stencil.

7.2.2 Each container of acetic anhydride shall bear the label given in Fig. 7 of IS: 1260-1958*. The lower half of the label shall have the following words printed in red letters. Any other label or warning or other statement required by statutes, regulations or ordinance may also be used in combination or separately.

ACETIC ANHYDRIDE

DANGER: Flammable, causes severe burns.

Do not get liquid or vapour into eyes, on skin or clothing.

Keep away from heat and open flame.

In case of contact, immediately flush skin or eyes with plenty of water for at least 15 minutes.
Get medical attention.

8. GENERAL PREVENTIVE MEASURES

8.0 General — Acetic anhydride may be handled safely, provided workers so engaged are fully and adequately instructed and are supervised in approved and safe methods of handling.

*Code of symbols for labelling of dangerous goods.

8.1 Employee Selection and Training—Prior to assignment to processes involving the handling of acetic anhydride, all individuals should have a careful preplacement physical examination, and, in order to properly protect their health, those who have the following conditions should be excluded from such processes:

- a) Chronic skin conditions,
- b) Chronic diseases of the upper respiratory tract and chronic lung diseases such as asthma,
- c) Only one functioning eye, and
- d) Uncorrected severe faulty vision.

8.1.1 Employees should be instructed primarily in regard to the corrosive properties of acetic anhydride and its exothermic reaction with water.

8.1.2 Employees should be thoroughly familiar with the location of safety showers, fountains for eye-washing, and other protective service installations.

8.1.3 If water is inadvertently introduced into acetic acid, the vessel should immediately be vented to prevent pressure build up, protection should be provided against acetic anhydride liquid and vapour that may boil out of the vent, and the material cooled if provisions are available. If a heat exchanger is not available for cooling, it will be helpful if part of the material can be pumped into another acetic anhydride storage vessel, since heat will be dissipated faster and there is less chance of boiling over from a vessel that is only partially full. The same precaution should be exercised in the second vessel with respect to venting and precautions taken to prevent damage or injury if boil-over does occur.

8.1.4 Instructions should be given regarding personal protective equipment, the necessity of using it and its availability.

8.1.5 All employees who work constantly in processes involving acetic anhydride should have a careful physical examination at least once a year.

8.2 Personal Protective Equipment

8.2.1 Emergencies should be anticipated and proper personal protective equipment in sufficient quantities should be strategically located throughout the premises to be readily available in case of need. It should be examined and tested regularly and maintained in good condition at all times.

8.2.2 Eye Protection

8.2.2.1 Cup-type or rubber framed goggles, equipped with the approved impact resistant glass or plastic lenses, should be worn whenever there is danger of acetic anhydride coming in contact with the eyes.

8.2.2.2 Metal or plastic rim safety spectacles with unperforated side shields which can be obtained with prescription safety lenses or suitable all plastic safety goggles may be used where continuous eye protection is desirable, as in laboratories. These types, however, should not be used where complete eye protection against acetic anhydride is needed.

8.2.2.3 Plastic shields with forehead protection may be worn in addition to chemical safety goggles where complete face protection is desirable. Chemical safety goggles should always be worn as added protection where there is danger of material striking the eyes from underneath or around the sides of the face shield.

8.2.3 *Respiratory Protection* — Severe exposure to acetic anhydride may occur during equipment cleaning and repairs, when decontaminating areas following spills, or in case of failure of piping or equipment. Employees who may be subject to such exposures should be provided with proper respiratory protection and training in its use and care.

8.2.4 *Head Protection* — 'Hard' hats should be worn where there is danger from falling objects. If hard hats are not considered necessary, soft-brimmed hats or caps may be worn to give protection against liquid leaks and splashes.

8.2.5 *Foot Protection* — Leather or rubber safety shoes with built-in steel toe caps are recommended for workers handling drums and cans of acetic anhydride. Rubbers may be worn over leather safety shoes. Rubbers and shoes should be thoroughly cleaned and ventilated after contamination. Contaminated shoes should be removed immediately.

8.2.6 *Body, Skin and Hand Protection* — Sustained or intermittent skin contact with liquid acetic anhydride may produce dermatitis at the site of contact. It is imperative that contaminated clothing be removed promptly and laundered or thoroughly dried before re-use. Affected areas of the body should be washed thoroughly with soap and water (except the eyes which should be washed with water).

8.2.6.1 Clothing made of rubber or other impervious material may be worn to protect body against acetic anhydride splashes. Rubber gloves may be used for hands. These shall have to be cleaned inside and out after each use.

8.3 Safety Showers and Eye Baths

8.3.1 Rapid action and readily accessible safety showers shall be provided in the areas where acetic anhydride is being handled. These should be examined and tested regularly and maintained in working condition at all times.

8.3.2 A special eye washing fountain, a ready source of running tap water, a bubbler drinking fountain, or a hose with a soft, gentle flow of drinking water shall be provided for eye irrigation. It should be frequently inspected and maintained in good working condition at all times.

9. FIRST-AID

9.1 Contact with Skin—Whenever acetic anhydride comes in contact with skin *the speed in removing it is of primary importance*. First-aid shall be started immediately, as delay in initiating treatment may result in injury.

9.2 Apply copious quantity of running water. This can best be accomplished while the man is under a safety shower. All contaminated clothing shall be removed immediately.

9.3 In case of severe or extensive burns, symptoms of shock, such as rapid pulse, sweating, etc., may appear at any time. The patient should be kept in supine position (lying down on his back) and a physician should be called.

9.4 No oil or ointment should be applied to the affected areas without specific directions from the physician.

9.5 Contact with Eyes—If even minute quantities of acetic anhydride enter the eyes, they should be immediately irrigated with copious quantity of running water for 15 minutes. The eyelids should be held apart during the irrigation to ensure contact of water with all the tissues of the surface of the eyes and lids. A physician, preferably an eye specialist, should be called in attendance at once. If a physician is not immediately available, the eye irrigation should be continued for a second period of 15 minutes. Upon completion of the 15 minutes of ingestion, it is permissible to instil 2 or 3 drops of an effective aqueous local anesthetic for relief of pain. No oils or oily ointments should be instilled unless ordered by the physician.

9.6 Ingestion—Ingestion of acetic anhydride causes severe burns of the mucous membrane of the mouth, throat, and stomach. Do not attempt to induce vomiting. *Do not give anything orally to an unconscious patient*. If the patient is conscious, encourage him to wash out his mouth with water, give him milk with white of eggs to drink. If these are not immediately available, give as much water as possible for drinking. A physician should be called at once.

9.7 Inhalation—A worker who has been overcome by acetic anhydride vapours should be removed immediately from exposure to a fresh or an uncontaminated atmosphere. If breathing has stopped, an effective means of artificial respiration should be initiated immediately. If oxygen inhalation apparatus is available, oxygen should be administered, but only by a person authorized for such duty by a physician. A physician should be called at once. The patient should be kept comfortably warm, but not hot.

10. CLEANING AND REPAIRS OF TANKS

10.1 Preparation of Tanks and Equipment

10.1.1 Tank and equipment cleaning should be done under the direction of thoroughly trained personnel who are fully familiar with all of the hazards and the safeguards necessary for the safe performance of their work.

10.1.2 Tanks and equipment, pumps, lines and valves should always be drained and thoroughly flushed with water before being repaired. Workmen should never be allowed to attempt to repair equipment while it is in operation and the lines full. If pipe sections are to be removed and flanges opened, the lower bolts should be loosened first and although the lines have been flushed, care should be taken to avoid personal contact with the liquid draining, or dripping from the equipment. All spillage from the lines or equipment should be removed immediately by flushing to the drain with large quantities of water.

10.1.3 The tank or equipment to be repaired should first be emptied of all liquid, and all pipes leading to and from the tank (except vents) after draining should be disconnected or blanked off.

10.1.4 The tank should be steamed to remove residual acetic anhydride and vapours. Steam lines should be large enough to raise the tank temperature above the boiling point of acetic anhydride and the steaming should be continued until the acetic anhydride vapours have been removed.

10.1.5 The tank should then be cooled, preferably by filling with water and draining once or twice.

10.1.6 The tank should then be purged with fresh air and the air should be tested for acetic anhydride vapour by an approved method before permitting personnel to enter.

10.2 Entering Tank

10.2.1 No one should enter a tank or confined space until a work permit has been signed by an authorized person indicating that the area has been tested for oxygen deficiency and explosive concentration and found to be safe. Furthermore, no workman should enter a tank or vessel that does not have a manhole opening large enough to admit a person wearing an acid resistant safety harness, life line, and emergency respiratory equipment. It should be ascertained that the tank or vessel can be left by the original entrance.

10.2.2 One man on the outside of the tank should keep the man in the tank under observation and another man should be available nearby to aid in rescue if any of the man in the tank are overcome.

10.3 Ventilation

10.3.1 A supplied-air respirator or self-contained breathing apparatus, together with rescue harness and life line should always be located outside the tank entrance for rescue purposes, regardless of the type of respiratory equipment or air supply which is provided for employees inside the tank.

10.3.2 Special ventilation is recommended during the entire time men are cleaning, repairing, or inspecting the tank. Ventilation can be accomplished by exhausting or removing vapours from the bottom of the tank either through its bottom openings, or by exhausting the vapours from the tank bottom by means of large flexible ducts where tanks have top openings only. The blowers or air movers used for ventilation to ensure against oxygen deficiency should be sparkproof and should be grounded. They should be cleaned frequently so that moving parts will not set up frictional heat which may cause ignition of the vapour.

11. WASTE DISPOSAL

11.1 Small Quantities — Disposal may be accomplished by removal of the wastes to a safe location away from buildings or other combustible structures, pouring the mixture on dry sand or ashes, and then cautiously igniting it. Small quantities may also be washed down the drain provided that the piping is corrosion resistant.

11.2 Larger Quantities

11.2.1 If larger quantities of this material are spilled, the supplier should be called for advice on emergency methods to dispose of it, since the recommended method may depend on the circumstances.

11.2.2 Waste mixtures containing acetic anhydride should not be allowed to enter those drains or sewers where there might be danger of the vapour becoming ignited.

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